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Flow Through Submerged Orifices

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From the measurements of F. E. Giesecke on the flow of liquids through submerged orifices two definite laws have been deduced. When the diaphragm is completely closed, the liquid flows backwards along the wall of the tube, and forward in a central vein, the radius of which has been calculated for laminar and turbulent flow. The theory by v. Kármán for turbulent flow has been applied to a tube of circular cross section. It is shown that both the backward flow and the jet issuing from the orifice are unstable. By an experiment it is made evident that a jet may sometimes describe a spiral motion.

PROFESSOR F. E. Giesecke[1] has made very careful measurements of the flow of water through submerged orifices, from which definite laws can be deduced. He measured the loss of head as a function of the velocity and of the diaphragm, shown in Fig. 1. The diameter of the pipe was 2.65 cm, the diameter of the orifice varied from 0.75 to 2 cm, and the velocity of the water varied between 2 to 200 cm per second. The results were plotted in logarithmic coordinates. Using, however, ordinary coordinates, drawing as abscissae the square of the velocities, v^2, and as ordinates the loss of head Δh, I find the straight lines of Fig. 2, according to which

$$\Delta h = Cv^2, \tag{1}$$

a law which follows immediately from the principle of dimensional homogeneity. The straight lines of Fig. 2 correspond to the various diameters of the diaphragm, from 0.4 to 0.8 inch.

If I plot on logarithmic coordinate paper the loss of head Δh as function of the diameter, then I find the curves of Fig. 3, which are nearly straight lines showing, however, a slight curva-

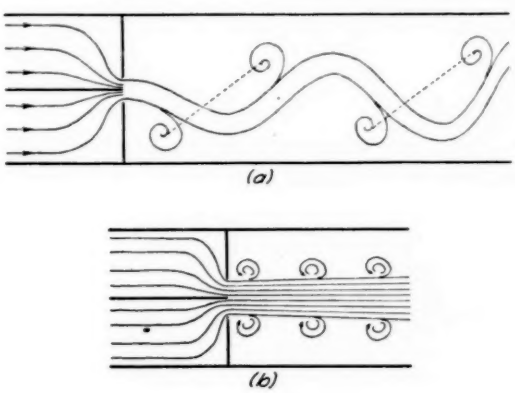

FIG. 1.

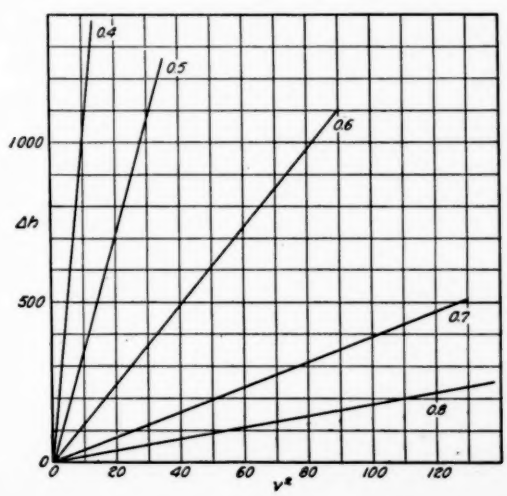

FIG. 2.

[1] F. E. Giesecke, "Loss of Head in Submerged Orifices," *Heating, Piping and Air Conditioning*, Vol. 2 (1930), p. 611.

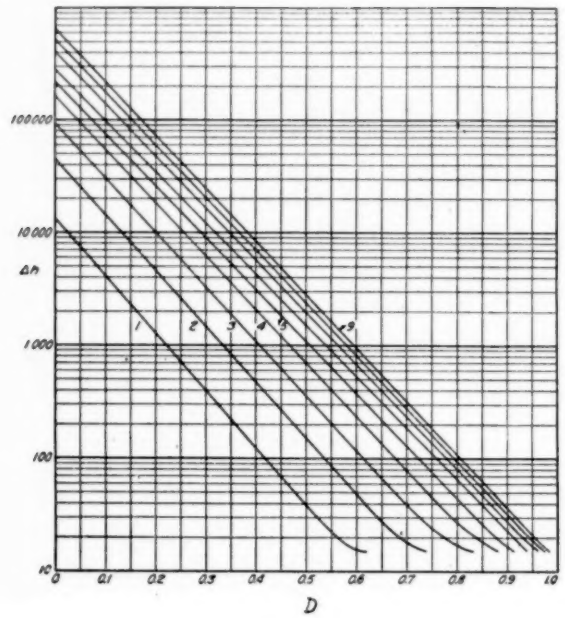

FIG. 3.

ture for small values of Δh. These curves represent Δh for various velocities. The straight line part of these curves can be represented by $\log \Delta h = -ax+b$ or ($x = D =$ diameter); or

$$\Delta h = \Delta h_0 e^{-aD}. \tag{2}$$

Combining Eqs. (1) and (2) we obtain

$$\Delta h = Cv^2 e^{-aD}, \tag{3}$$

where C is a constant and $a = \tan \alpha$ is the slope of the curves of Fig. 3. The average value of α is 73° 15′, hence $a = \tan \alpha = 3.32$. When the straight lines of Fig. 3 are prolonged until they intersect the axis of ordinates, we find the points corresponding to the loss of pressure when the diaphragm is closed; it is easily found that $\Delta h/v^{1.76}$ is constant. But $1.75 = 7:4$ and Prandtl's theory of turbulent motion gives for the shearing force τ_0 at the wall of the tube:

$$\tau_0 = C\rho\nu^{\frac{1}{4}}r^{-\frac{1}{4}}v^{7/4}.$$

If the diaphragm is completely closed, then the pressure increases and a pressure wave travels through the liquid column, with the velocity of sound; but there is also another phenomenon recently observed by E. E. Ambrosius and J. C. Reed, namely, the liquid returns at the diaphragm and moves along the wall of the tube in a direction opposite to the original motion in the center. Let in Fig. 4 the radius of the tube be R, the radius of the central bore be r_1, its average velocity be $\bar{u}_1$ and the average velocity over the tubular cross section $\pi(R^2-r_1^2)$ be $\bar{u}_2$, then when the diaphragm is closed, we must have in every cross section

$$\pi r_1^2 \bar{u}_1 = \pi(R^2-r_1^2)\bar{u}_2, \tag{4}$$

expressing the fact that the resultant flow through any cross section is zero.

If we assume at first laminar flow, we have for the steady state of flow

$$u = \frac{p_1 p_2}{l}\frac{1}{4\eta}(R^2-r^2). \tag{5}$$

The maximum velocity u_m in the center of the circular cross section is equal to

$$u_m = \frac{p_1-p_2}{l}\frac{1}{4\eta}R^2,$$

while the average velocity $\bar{u}$ is equal to

$$\bar{u} = \frac{p_1-p_2}{l}\frac{R^2}{8\eta} = \frac{u_m}{2}. \tag{6}$$

The profile of the motion is a parabola, shown in Fig. 5. For a certain radius r_1 the velocity is

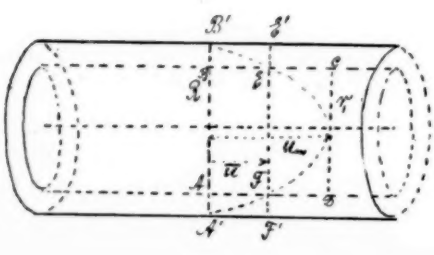

FIG. 4.

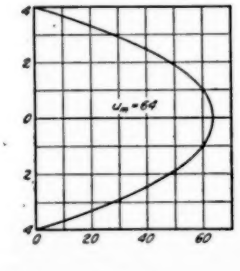

FIG. 5.

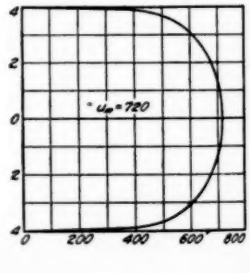

FIG. 6.

equal to the average velocity. This radius is determined by (5) and (6) as

$$R^2-r_1^2=R^2/2, \quad \text{or} \quad r_1^2=R^2/2. \tag{7}$$

Using (6) and (7) we obtain the difference

$$u_m\pi r_1^2-\bar{u}\pi(R^2-r_1^2)=2\bar{u}\pi r_1^2-\bar{u}\pi(r_1^2)=\bar{u}\pi r_1^2.$$

The volume of the cylinder (Fig. 4) ($ABCD$) minus the volume of the ring (AA', BB', EE', FF') is equal to the volume of the cylinder $ABEF$, but this is also equal to $ABCD-EFCD$; hence the volume of $EFCD$ is equal to the volume of AA', BB', EE', FF'. If we therefore assume that $\bar{u}$ over the ring $AA'\,BB'$ is equal and opposite to $\bar{u}$ over the circular cross section πr_1^2, then the average resultant velocity through the whole cross section is zero; in other words, the average velocity $\bar{u}_1$ must be equal to $\bar{u}_2=\bar{u}$ in formula (4) which then reduces to an identity. We have therefore immediately after closing the diaphragm

$$r_1=R/\sqrt{2}=R\cdot 0.71. \tag{8}$$

Hence the mass which flows through $\pi(R^2-r_1^2)$ backwards, is equal to the mass which flows forward through πr_1^2; hence also the average momentum and the average energy through the two cross sections per unit time is the same.

But the average velocity $\bar{u}$ cannot remain constant, because the energy will gradually and even rapidly become dissipated in the form of heat. Indeed, the work done by the forces of friction per unit time and unit volume will be equal to

$$dW/dt=\bar{u}\partial p/\partial x=\eta 8\pi\bar{u}^2/\pi R^2,$$

and per unit length equal to $\pi R^2\bar{u}\partial p/\partial x=\eta 8\pi\bar{u}^2$ and the work done through dx per unit time will be $dW=8\pi\eta\bar{u}^2dx$, or $dW/dx=8\pi\eta\bar{u}^2$ is equal to the decrease of the kinetic energy per unit time of the volume $\pi R^2\cdot 1$, which gives

$$8\pi\eta\bar{u}^2=-(d/dt)(\rho\pi R^2\bar{u}^2);$$

hence

$$\bar{u}^2=\bar{u}_0^2e^{-16\eta t/\rho R^2}. \tag{9}$$

We can also find the decrease of the average velocity along the axis of the tube in the following way. The difference in kinetic energy entering and leaving the volume $dx\pi R^2$ per unit time is equal to the kinetic energy in this volume transformed in heat. The entering kinetic energy is equal to $\pi R^2(\rho/2)\bar{u}^2\bar{u}$; the kinetic energy leaving is equal to $\pi R^2(\rho/2)(\bar{u}+\partial\bar{u}\partial x/dx)^2(\bar{u}+\partial\bar{u}dx/\partial x)$; the difference is equal to $(-3\pi R^2\rho u^2/2)(\partial u/\partial x)dx$, and this is transformed into heat. $[8\pi\eta\bar{u}^2dx]$, hence $\bar{u}=-16\eta x/3\rho R^2+\bar{u}_0$. We shall see moreover that this sort of laminar motion is unstable. But before considering that problem, we shall consider the steady turbulent flow in a tube of circular cross section with radius R. If we apply the theory of turbulent flow of Th. v. Kármán[2] to a tube, then we obtain the formula

$$u=u_m+\frac{1}{k}(\tau_0/\rho)^{\frac{1}{2}}[\log(1-(r/R)^{\frac{1}{2}})+(r/R)^{\frac{1}{2}}], \tag{10}$$

where k is a constant between 0.36 and 0.4; ρ is the density, τ_0 the shearing stress at the surface; the average velocity then becomes equal to

$$\bar{u}=\frac{1}{\pi R^2}\int_0^R u2\pi r dr=\frac{2}{R^2}\int urdr$$

$$=\frac{2}{R^2}\int u_m r dr+\frac{2}{R^2}\frac{1}{k}(\tau_0/\rho)^{\frac{1}{2}}\int[\log(1-(r/R)^{\frac{1}{2}})+(r/R)^{\frac{1}{2}}]rdr.$$

Integrating by expansion in a series, I obtain

$$u=u_m-\frac{4}{k}\left(\frac{\tau_0}{\rho}\right)^{\frac{1}{2}}\left\{-\frac{1}{5}+\frac{1}{1.5}+\frac{1}{2.6}+\frac{1}{3.7}+\cdots\right\}$$

but

$$\sum_1^\infty\frac{1}{n(n+4)}=\frac{1}{4}\sum_1^\infty\left(\frac{1}{n}-\frac{1}{n+4}\right)$$

$$=\frac{1}{4}\left[\frac{1}{1}+\frac{1}{2}+\frac{1}{3}+\frac{1}{4}+\frac{1}{5}+\frac{1}{6}+\cdots-\frac{1}{5}-\frac{1}{6}\right]\cdots$$

$$=\frac{1}{4}\left(\frac{1}{1}+\frac{1}{2}+\frac{1}{3}+\frac{1}{4}\right)=\frac{25}{48}, \quad \text{hence}$$

$$\bar{u}=u_m-\frac{4}{8}\left(\frac{\tau_0}{\rho}\right)^{\frac{1}{2}}\left(-\frac{1}{5}+\frac{25}{48}\right)$$

$$=u_m-\frac{77}{60}\frac{1}{k}\left(\frac{\tau_0}{\rho}\right)^{\frac{1}{2}}. \tag{11}$$

[2] Th. v. Kármán, *Nachrichten d. Ges. d. Wiss. Göttingen* (Jan., 1930), p. 58.

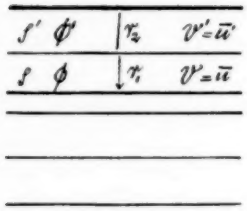

FIG. 7.

This average value $\bar{u}$ is equal to u at a distance r_1 from the center, where r_1 is determined by the equation

$$ur_1=\bar{u}=u_m+\frac{1}{k}\left(\frac{\tau_0}{\rho}\right)^{\frac{1}{2}}\left[\log\left(1-\left(\frac{r_1}{R}\right)^{\frac{1}{2}}\right)+\left(\frac{r_1}{R}\right)^{\frac{1}{2}}\right]$$

$$=u_m-\frac{77}{60}\frac{1}{k}\left(\frac{\tau_0}{\rho}\right)^{\frac{1}{2}}$$

or by the equation

$$-\frac{77}{60}=\log\left(1-\left(\frac{r_1}{R}\right)^{\frac{1}{2}}\right)+\left(\frac{r_1}{R}\right)^{\frac{1}{2}}=-1.28.$$

Solving this transcendental equation for r_1 I find by trial and error

$$r_1=R\cdot 0.766, \tag{12}$$

instead of the value for r_1 for laminar motion given in Eq. (8). The profiles of the laminar and the turbulent motion are given in Figs. 5 and 6 for maximum velocities of 64 and 720, respectively. Extrapolated from the tables of I. Nikuradse,[3] $\tau_0/\rho=965$.

If a flowing column of water is suddenly stopped, it has been assumed that the whole kinetic energy per unit volume $1/2\ m\bar{u}^2$ is transformed into elastic energy of compression, the pressure increase Δp at the diaphragm being given by

$$\Delta p=\Delta V\cdot K=p-0=p,$$

where K is the coefficient of compressibility, and ΔV the change of the volume. The conservation of energy gives:

$$\tfrac{1}{2}m\bar{u}^2=\bar{p}\Delta V, \quad \text{but} \quad \bar{p}=p/2$$

$$=\tfrac{1}{2}p\cdot p/K=p^2/2K$$

or

$$p=\bar{u}\left(\frac{K}{m}m\cdot m\right)^{\frac{1}{2}}=\bar{u}m(V_s)^{\frac{1}{2}}, \tag{13}$$

where $V_s=(K/m)^{\frac{1}{2}}$ is the velocity of sound in the column, p is the sudden pressure increase at the diaphragm. Now the question arises, whether this pressure increase is the same, when the liquid turns around and moves backwards. We have seen that the kinetic energy, flowing through any cross section πR^2 is equal to zero, so that indeed the whole original kinetic energy before closing the valve is transformed again into elastic energy of compression according to Eq. (13) though from an analogy with a solid elastic body, rebounding from a rigid wall it might appear at a first thought that the pressure p might be twice as large. But the analogy is not complete, because in the case of the moving liquid column only one-half of the water rebounds.

We have considered one liquid column flowing inside another one in opposite direction. Such a motion is unstable. This follows from Rayleigh's[4] criterion of stability of jets, applied to our present problem. We consider two coaxial cylinders of liquids, (Fig. 7) the outer one having the density ρ', the velocity V' and the velocity potential

$$\phi'=C'\cosh k(r-r_2)e^{i(\omega t+kx)},$$

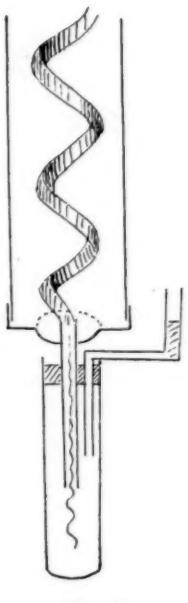

FIG. 8.

[3] I. Nikuradse, Forschungsarbeiten **289**, 38 (1927).

[4] Rayleigh, *Theory of Sound*, Vol. 2, p. 378.

while for the inner cylinder

$$\phi = C \cosh k(r+r_1)e^{i(\omega t+kx)},$$

and the disturbance at the boundary h is equal to $h=He^{i(\omega t+kx)}$), $k=2\pi/\lambda$, $\omega=2\pi\nu$, where ν is the frequency, λ the wave-length; then the motion is stable if

$$(g(\rho-\rho')+k^2T)(\rho \cot hkr_1+\rho' \cot hkr_2)$$
$$-k\rho\rho' \cot hkr_1 \cot hkr_2(V-V')^2>0.$$

T is the surface tension between the two non-viscous liquids, g the acceleration of gravity. In the present case $\rho=\rho'$, $T=0$, $V=V'$, hence the condition of stability cannot be satisfied for any value of λ. Even if V were not equal to $-V'$, and if λ were very small, still no stability would obtain. This conclusion also holds for the jet, issuing from the submerged orifice. These phenomena have recently been studied by Ambrosius and Reed. Behind the orifice there appears for small velocities a system of small vortices accompanying the central jet, shown in Fig. 1b. For higher velocities the central jet begins to oscillate, showing a system of vortices, Fig. 1a, which reminds me somewhat of the vortex ally of v. Kármán. But it may be that there are vortex rings surrounding the central jet, vortex rings whose axes are inclined toward the direction x of the general motion. These vortices disappear gradually as the liquid flows downward, giving rise to steady turbulent motion. It is also possible to imagine that the central jet describes a spiral motion. In order to test this possibility, an experiment was made which is illustrated by Fig. 8. A test tube is filled with turpentine; a wick, passing through a capillary tube, burns with a small steady flame in the lower end of a glass tube of 5 cm diameter and 30 cm length. A very narrow column of smoke rises from the flame, often showing a spiral motion. Sometimes the jet forms a ribbon, which appears twisted like an elastic band.

Viscous Properties of Polyisobutylene

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The viscosity of polyisobutylene (molecular weight about 4900) has been studied from 70°C to 175°C with a falling sphere viscometer and from −53°C to 24°C with a concentric cylinder viscometer. In the measurements with the latter apparatus, elastico-viscous effects appeared, and the viscous behavior was non-Newtonian. The apparent viscosities were accordingly extrapolated to zero torque to give values for the viscosity at zero shear. The viscosity ranges from 19 poises at 175°C to 10^{10} poises at −53°C, showing a rather low temperature coefficient. At −76°C, the midpoint of the "transition region" for polyisobutylene glass, the viscosity has an extrapolated value of about 10^{13} poises, in agreement with a general rule for glass-forming materials. Macroscopic and microscopic interpretations of viscosity anomalies are discussed.

INTRODUCTION

POLYMERIC organic compounds whose molecules are supposed to have the form of prolonged chains of repeated units have been the subject of much experimental study in dilute solution. Among the properties of these linear macromolecules which have been investigated are diffusion,[1] streaming double refraction,[2] sedimentation,[3] and dipole moments.[4] Above all, the effect of long, rod-shaped molecules on the viscosity of a solvent has been extensively studied experimentally[5, 6] and has been given considerable theoretical treatment.[7] On the other hand, the physical properties of the pure polymers in the absence of solvent have received little attention.

In connection with an investigation[8] of the physical properties of a sample of polyisobutylene, with special attention to the formation of a glass at low temperatures, we have studied the viscosity of this substance in the pure form over a range of temperature from −53°C to 175°C. Measurements were made by the falling sphere method and by the Couette or concentric cylinder method. These viscosity determinations were undertaken for comparison with previous measurements on other glass-forming liquids[9, 10] of simple molecular structure and low molecular weight.

The present study also provides examples of anomalous or "non-Newtonian" viscous behavior. In the temperature range in which the concentric cylinder method was applied, the apparent viscosity for a given temperature and torque was a function of the time (due to elastic effects), approaching a constant value (cf. Filon and Jessop,[11] Stott,[12] and Umstätter[13]); whereas the final, constant value was, at a given temperature, a function of the torque applied (cf. Reiner,[14] Lawrence,[15] and Philippoff[16]).

MATERIAL

The sample of polyisobutylene used in this work had an average molecular weight of 4900 as determined by cryoscopic measurements in benzene solution; actually the sample was a mixture of polymers with a wide range of molecular weights.

The molecules of polyisobutylene, like those of other linear polymers, are generally supposed to be unbranched chains of great length. This hypothesis, while not at present susceptible to

* Shell Research Fellow at Stanford University for the academic year 1934–35.

[1] R. O. Herzog and H. Kudar, Zeits. f. physik. Chemie **A167**, 343 (1934).

[2] R. Signer and H. Gross, Zeits. f. physik. Chemie **A165**, 161 (1933).

[3] E. O. Kraemer and W. D. Lansing, J. Am. Chem. Soc. **55**, 4319 (1933); J. Phys. Chem. **39**, 153 (1935).

[4] W. Gallay, Koll. Zeits. **57**, 1 (1931).

[5] H. Staudinger, *Die Hochpolymeren Organischen Verbindungen* (Julius Springer, Berlin, 1932).

[6] E. O. Kraemer and F. J. Van Natta, J. Phys. Chem. **36**, 3175 (1932).

[7] E. Guth and H. Mark, Ergeb. d. exakt. Naturwiss. **12**, 115 (1933).

[8] J. D. Ferry and G. S. Parks, to be published in the J. Chem. Phys.

[9] G. S. Parks, L. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).

[10] G. S. Parks and M. E. Spaght, Physics **6**, 69 (1935).

[11] L. N. G. Filon and H. T. Jessop, Phil. Trans. Roy. Soc. **A223**, 89 (1922).

[12] V. H. Stott in W. S. Turner, *The Constitution of Glass* (Society of Glass Technology, Sheffield, 1927), pp. 73, 155.

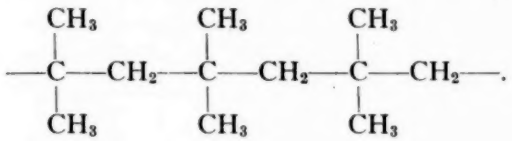
[13] H. Umstätter, Koll. Zeits. **70**, 174 (1935).

[14] M. Reiner, Physics **5**, 321 (1934).

[15] A. C. S. Lawrence, Proc. Roy. Soc. **A148**, 59 (1935).

[16] W. v. Philippoff, Koll. Zeits. **71**, 1 (1935).

proof, is supported by the above-mentioned studies in dilute solution,[1, 2, 5, 6] especially those of Staudinger. The most probable arrangement for the isobutylene units in polyisobutylene is



If bond lengths and angles are the same as in normal paraffins, a molecular weight of 4900 corresponds to a length of about 220A. However, more complicated arrangements may also be involved, with side chains longer than the methyl groups.

The density of our sample, determined at three temperatures, is given in Table I.

TABLE I. *Density of polyisobutylene.*

Temperature	23.4°C	100.2	178.2
Density	0.9074 g/cm³	0.873	0.835

MEASUREMENTS BY THE FALLING SPHERE METHOD

Viscosity determinations over the temperature range from 70°C to 175°C were carried out by the falling sphere method, with the same apparatus previously employed for measuring the viscosity of glucose.[9] The formula of Ladenburg,[17] in which the effect of the sides and ends of the cylindrical column of liquid is taken into account, was used to evaluate the viscosity from the measured rates of fall of steel bearing-balls.

Under the circumstances of these experiments, there was no evidence for non-Newtonian viscous behavior. Comparative determinations at the same temperature with different sizes of balls agreed within experimental error; and successive determinations at the same temperature showed no trend indicative of irreversible changes or persistent anisotropic arrangements induced by the motion of the spheres. It was concluded, therefore, that a Newtonian flow obtained, and that the quantities calculated by application of the Ladenburg formula represented "true" viscosities.

Over seventy individual determinations were made in the given temperature range. In a plot of the logarithm of viscosity against temperature, most of the points fell within a distance from the smooth curve which corresponded to a deviation in the viscosity of 4 percent. Measurements made before and after heating to the highest temperature employed (175°C) were in satisfactory agreement, showing that no decomposition or oxidation sufficient to affect the viscosity was occasioned by the heating. Duplicate determinations were also made at 21°C and were in reasonable agreement with the results from the concentric cylinder measurements described below. Representative values of the viscosity and its logarithm are given in Table II. These values

TABLE II. *Viscosity of polyisobutylene by the falling sphere method.*

Temp. (°C)	Viscosity, η poises	$\log_{10}\eta$	Temp. (°C)	Viscosity, η poises	$\log_{10}\eta$
21	5.8×10^4	4.76	120	1.26×10^2	2.10
70	1.63×10^3	3.21	130	85	1.93
80	9.1×10^2	2.96	140	59	1.77
90	5.1×10^2	2.71	150	42	1.62
100	3.1×10^2	2.49	160	30	1.48
110	1.9×10^2	2.28	170	22	1.35

are represented in Fig. 4 by the unbroken portion of the curve, the scale being too small here to show the individual determinations by the falling sphere method; except those at 21°C, which are represented by a triangular point.

MEASUREMENTS BY THE CONCENTRIC CYLINDER METHOD

No determinations of viscosity were made between 24°C and 70°C. Below 24°C, measurements were carried out by the Couette or concentric cylinder method.

Apparatus

The apparatus employed was very similar to that previously used in the studies on glucose,[9] but modified to permit measurements at low temperatures. A Pyrex test-tube (internal diameter 2.27 cm) and a hollow steel rod (diameter 0.95 cm) constituted the outer and inner cylinders, respectively; the latter was immersed in the polyisobutylene to a depth of about 7 cm. Temperature control was accomplished by a double jacket consisting of two cylindrical copper buckets separated by an air gap of 1 cm. The

[17] R. Ladenburg, Ann. d. Physik (4) **23**, 447 (1907).

inner jacket, which was equipped with an adequate stirrer and a heating coil, contained a bath of ethyl alcohol surrounding the Pyrex test-tube. The outer jacket was suspended in a 3-liter Dewar jar, and was packed with ice or with carbon dioxide snow. The whole arrangement was rigidly attached to a small rod of channel iron, the bearings of the rotor or inner cylinder being accurately centered. To minimize leakage of heat down the channel iron into the bath, the apparatus was enclosed in a cabinet of Celotex. In order to attain the lowest temperatures, small quantities of liquid air were introduced into the space between the two copper jackets. The lowest temperature at which a viscosity measurement was made was −53°C. The lowest temperature at which satisfactory thermal equilibrium could be maintained for a period of an hour or two (long enough for a complete series of determinations for a consistency curve) was −43°C. The temperature of the bottom of the steel rotor was measured by a copper-constantan thermocouple in connection with a White potentiometer. A similar thermocouple measured the temperature of the alcohol bath in the inner jacket.

Torque was applied to the inner cylinder by exerting a force at the rim of a wheel of known dimensions. This force was supplied by a weight attached to a thread which was wound around the wheel and passed over a pulley. The problem of the frictional drag of the rotor bearings was considered carefully. The apparatus was calibrated when empty by weighting equally both ends of a thread wrapped around the wheel, and determining the additional weight required to be added to one end to overcome frictional resistance to turning. The frictional moment was found to be separable into two terms, the first independent of load (attributed to the vertical reaction on the bearings) and the second proportional to the total load and amounting to 6 percent of it (attributed to the horizontal reaction on the bearings). In all viscosity determinations, the data were corrected by subtracting from the actual moment applied the corresponding frictional moment.

Other details of construction and operation of the viscometer were similar to those in the glucose study previously mentioned. The usual formula employed for calculation of the viscosity is

$$\eta = kC/\omega, \tag{1}$$

where C is the applied torque, ω the angular velocity of the rotor, and k is a constant calculable from the dimensions of the apparatus.[9] This equation depends on the assumption that Newtonian flow obtains. In the case of non-Newtonian flow, as in the present experiments, application of the formula gives "apparent viscosity" values. The latter probably do not describe the fundamental viscous properties of the material, but show only how it behaves in the given type of experiment. A more fundamental quantity is the viscosity at zero shear, obtained by extrapolation of the apparent viscosity, as explained below.

Dependence of deformation rate upon time: Elastico-viscous effects

Under a given load, the rate of turning was a maximum when torque was first applied to the rotor; it fell off with time to approach a steady value. This behavior was undoubtedly due to combined elastic and viscous displacements caused by the shearing stresses in the polyisobutylene (elastico-viscous effect[12]). When the torque was removed, the rotor "unwound" to a certain extent; the rate of this elastic return, also, was rapid at first and fell off with time asymptotically to zero.

In a few cases, the course of the initial elastic

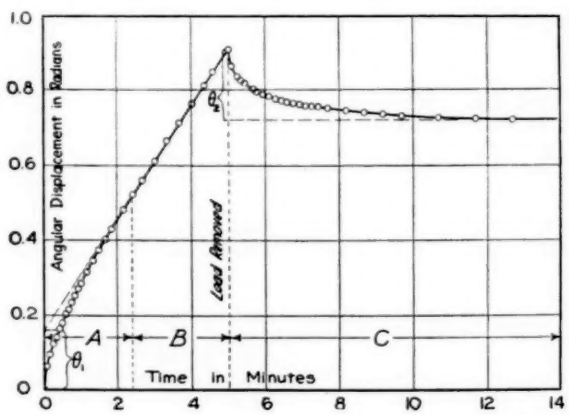


FIG. 1. Angular displacement of inner cylinder plotted against time, showing elastic effects. Portion A of the curve represents elastic and viscous displacement; portion B, viscous displacement alone; and portion C, elastic return.

deformation when the torque was applied and that of the final elastic return when the torque was removed were followed in detail.[18] Curves of angular displacement against time, plotted from these data, were all of the type shown in Fig. 1. Each curve consisted of a portion A representing combined elastic and viscous deformation, a portion B representing viscous deformation alone, and a portion C representing elastic return. In the majority of cases, however, no data were taken for the portions A and C of such curves. The load was simply applied for a time long enough to satisfy the elastic displacement, i.e., until successive determinations of the angular velocity of rotation were in agreement. At the lowest temperatures, it was necessary to wait as much as twenty minutes before the rate of rotation attained this stationary value (represented by the slope of portion B of the displacement-time curve).

Dependence of elastic effects upon torque applied

Extrapolation of the straight portion B of the displacement-time curve to zero time gives an angle θ_1, which represents the excess initial displacement over what would have occurred had the viscous flow of portion B been the only type of deformation from the start. This angle, θ_1, and that of the total elastic return upon removal of load, θ_2, are related to the elasticity of the material. The fact that the two are not found to be identical suggests that the elasticity of the flowing material is different from that of the material at rest. The dependence of θ_1 and θ_2 upon the applied torque is illustrated in Fig. 2, which gives data from a single series of experiments. The initial displacement, θ_1, is roughly proportional to the torque (corresponding to Hooke's law); the final elastic return, θ_2, is much smaller than θ_1 at low torques. Both quantities appear to fall off from the proportionality law at high torques, suggesting that some sort of elastic limit has been reached.

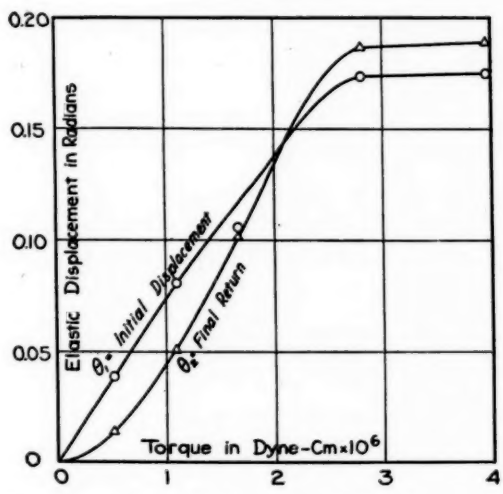


FIG. 2. Elastic displacement (initial and final) in radians, plotted against torque in dyne-cm. Temperature = 242.5°K.

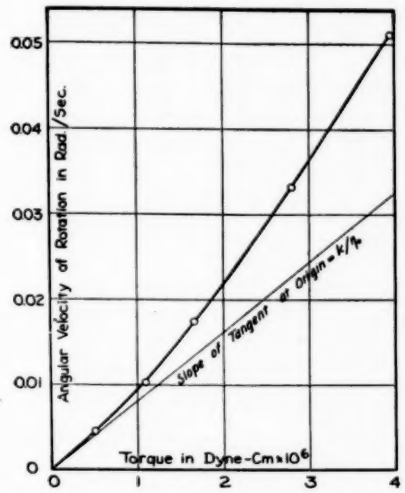


FIG. 3. Consistency curve for polyisobutylene: Angular velocity in radians per second plotted against applied torque in dyne-cm. Temperature = 257.8°K.

Dependence of apparent viscosity upon torque applied: Non-Newtonian flow

At a given temperature, the stationary value of angular velocity of turning was not proportional to the torque applied. Curves of angular velocity against torque were all of the type shown in Fig. 3, which represents a "consistency curve," in the terminology of Reiner,[19] and is a good example of non-Newtonian flow. In this diagram, apparent viscosities (η_C') are represented by the reciprocal slopes of lines drawn from the origin to the consistency curve (multi-

[18] We are indebted to Mr. B. L. Crawford, Jr., for assistance in some of these measurements.

[19] Reiner's "consistency curve" (reference 14) is actually a plot of rate of shear against shearing stress; in the Couette apparatus, these variables are proportional, respectively, to the angular velocity of turning and to the applied torque.

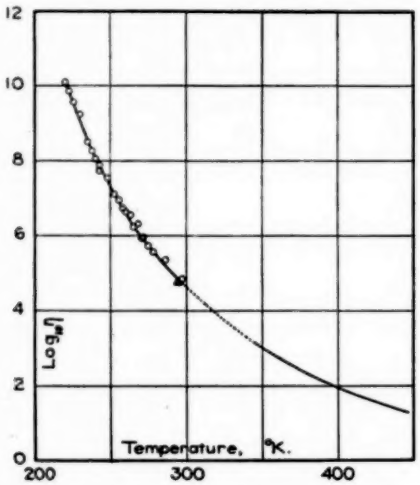


FIG. 4. The logarithm of the viscosity of polyisobutylene as a function of temperature. The circular points represent measurements by the concentric cylinder method; the unbroken line above 340°K and the triangular point, measurements by the falling sphere method.

plied by the apparatus constant, k). The viscosity of the material at zero shear is given by the reciprocal slope of the tangent to the consistency curve at the origin, multiplied by k.

The non-Newtonian flow of polyisobutylene is in marked contrast to the strictly Newtonian flow observed for other glass-forming liquids. whose consistency curves are straight lines passing through the origin.[9, 10]

The viscosity at zero shear is defined as

$$\eta_0 = \lim_{C\to 0} kC/\omega = \lim_{C\to 0} \eta_C' \qquad (2)$$

and is a property of the material at rest, in the absence of abnormal molecular arrangements induced by viscosimetric experiments. Hence this is the quantity to be compared with the viscosities measured at higher temperatures by the falling sphere method (where the shear was insufficient to occasion non-Newtonian effects), and with viscosities of Newtonian systems in general. Accordingly, at a number of temperatures, data for consistency curves were obtained, and values for η_0 were calculated by extrapolating η_C' to zero torque. The ratio η_C'/η_0 varied from 0.9 to 0.8 for the smallest torque used, and was as low as 0.3 for the greatest torque. The ratio η_C'/η_0 for a given torque varied less than 20 percent over a temperature range from 230°K to 270°K, in which η_0 varied two thousand-fold. At temperatures where no consistency curves were determined, the apparent viscosity η_C' for some given torque was corrected to give η_0 by a coefficient estimated from preceding and succeeding determinations.

Representative values for viscosity at zero shear

The final values of the logarithm of η_0 for twenty-three viscosity determinations by the concentric cylinder method, with two different portions of the polyisobutylene sample, are plotted in Fig. 4. Most of the points fall within a distance of the smooth curve corresponding to a deviation in the viscosity of less than 12 percent. Representative values of the zero-shear viscosity and its logarithm are given in Table III.

TABLE III. *Values of η_0 for polyisobutylene by the concentric cylinder method.*

TEMP. (°C)	η_0	LOG$_{10}$ η_0	TEMP. (°C)	η_0	LOG$_{10}$ η_0
−50	6.5×10^9	9.81	−10	2.5×10^6	6.40
−40	6.2×10^8	8.79	0	6.9×10^5	5.84
−30	7.6×10^7	7.88	10	2.3×10^5	5.36
−20	1.3×10^7	7.10	20	8×10^4	4.90

THE VISCOSITY-TEMPERATURE CURVE

The viscosity data obtained from both methods of measurement are plotted against the absolute temperature in Fig. 4, where the unbroken line above 340°K and the triangular point show the results of the falling sphere method, and the circles represent the values of η_0 from the concentric cylinder experiments. This curve has the same form as observed for other glasses,[9, 10] except that it is much less steep. The temperature coefficient of the viscosity of polyisobutylene is rather small; the quantity $d \ln \eta_0/d(1/T)$ is for polyisobutylene on the average only 0.3 that for glucose, and 0.4 that for boron trioxide (comparisons made at corresponding viscosities).

In the previous studies on glucose, boron trioxide, and glycerol[20] (in the last two cases by extrapolation from the measurements to lower temperatures), the viscosity of each of these glass-forming liquids was found to have a value of between 10^{13} and 10^{14} poises at the mid-

[20] G. S. Parks and W. A. Gilkey, J. Phys. Chem. **33**, 1428 (1929).

point of the "transition region" of temperature where the heat capacity and thermal expansion coefficient undergo sudden increases with rising temperature. This rule appears to hold irrespective of the nature of the material or of the mean temperature at which the transition takes place (513°K for boron trioxide; 187°K for glycerol). Measurements of the heat capacity and thermal expansion of polyisobutylene[8] place the midpoint of the transition interval for this material at 197°K (i.e., −76°C). Extrapolation of the viscosity curve to this temperature gives a value of $10^{13.2}$ poises. This conformity of polyisobutylene to the general rule is noteworthy, in view of its great molecular size and anisodimensionality (in contrast to the other glass-forming liquids), and its exhibition of non-Newtonian viscous behavior.

Discussion

The anomalous viscous phenomena exhibited by polyisobutylene have been observed for many other systems, and numerous formulations and interpretations have been put forward to describe them, without significant success. These theoretical treatments fall into two classes, the *macroscopic*, which consider only macroscopically measurable properties of the material in question, and the *microscopic*, which involve speculations concerning the microscopic structure of the material.

The starting-point of many of the macroscopic theories is the fundamental equation of Maxwell,

$$ds/dt=(1/E)dF/dt+F/\eta, \qquad (3)$$

where s is the deformation, F the force producing it, η the viscosity and E the elasticity. Under conditions where the two terms of the right member are of the same order of magnitude, "elastico-viscous" effects of the type observed (Fig. 1) are to be expected. They have been found for pitch,[21] glucose glass fibers,[22] silicate glasses,[12] and celluloid.[11] Quantitative inapplicability of the Maxwell equation is, however, shown by the fact that it predicts an exponential decay of elastic strains by viscous flow, whereas the observed decay does not follow an exponential law.[23] Umstätter,[13] starting from Eq. (3), deduced a completely opposite elastic effect from that observed for the above-mentioned substances; it should result in a rate of deformation which is low at first and rises to approach a steady value. Michelson[24] noted that the decrease in the rate of elastic deformation with time did not follow an ordinary exponential law, but that it could be fitted to an exponential law involving the square root of the time. The data for polyisobutylene fit this formulation fairly well, but its physical significance is obscure. Filon and Jessop[11] employed a formulation involving $t^{1/3}$, but it is purely empirical, and it does not give a deformation rate which approaches a constant value. Thompson[25] has derived an elaborate theory of visco-elasticity, satisfactorily tested by experiments on rubber. Unfortunately none of his formulations is applicable to our type of experiment (deformation under constant torque).

Eisenschitz[26] deduced from (3) that whenever $(F/E)^2$ was not negligible compared with unity, non-Newtonian flow should result, and the following expression should hold approximately:

$$\eta_F'/\eta_0=1/(1+F^2/E^2), \qquad (4)$$

where η_F' is the apparent viscosity for a force F. This formulation does not hold for the data on polyisobutylene, whose consistency curves (Fig. 3) cannot be fitted to an equation of the form $\omega=aC+bC^3$ (the equivalent of Eq. (4)). Besides, the ratio η'/η_0 has been found to vary but little with temperature, demanding by (4) a similar constancy in E; whereas as a matter of fact the latter varies considerably with temperature. Philippoff[16] modified the equation of Eisenschitz and introduced a new parameter, η_∞, the viscosity at infinite shear. However, the data for polyisobutylene cannot be well fitted to his formulation either.

The microscopic explanations for the origin of non-Newtonian flow have been summarized by Reiner.[14] Of his long list, the most important in

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[21] F. T. Trouton and E. S. Andrews, Proc. Phys. Soc. London **19**, 47 (1909).

[22] Unpublished experiments by Mr. J. D. Reagh in this laboratory.

[23] E. Hatschek, *The Viscosity of Liquids* (G. Bell and Sons, London, 1928), pp. 224–227.

[24] A. A. Michelson, J. Geol. **25**, 405 (1917).

[25] J. H. C. Thompson, Phil. Trans. Roy. Soc. **A231**, 339 (1933); J. C. Eccles and J. H. C. Thompson, Proc. Roy. Soc. **A148**, 171 (1935).

[26] R. Eisenschitz, Koll. Zeits. **64**, 184 (1933).

the case of polyisobutylene are probably orientation and stretching out of tangled macromolecules. Alignment of molecules in the lines of flow, either by orientation or by uncoiling and untangling, would diminish the viscous resistance to flow; and both these effects would increase with the shear, giving rise to a non-Newtonian consistency curve. More specifically, the orientation would depend on the rate of shear, and the stretching on the shearing stress. On the other hand, it seems probable that the elastic behavior is due to the stretching phenomena alone, and hence that the elastic properties and the viscous anomalies of the material do not have an identical microscopic origin, and cannot be connected so simply as Eisenschitz postulates.

The explanation of elastico-viscous effects for polyisobutylene cannot depend solely on its molecular size and anisodimensionality, because these effects occur in materials of simple molecular structure, such as glucose. However, a much greater shearing force is required to evoke elastico-viscous effects in glucose than in polyisobutylene; the elastic coefficient of polyisobutylene is rather smaller than those of other glass-forming liquids, compared at corresponding viscosities. It is possible that, at high shearing stresses, glucose would exhibit non-Newtonian flow; that is, the Eisenschitz criterion for existence of non-Newtonian behavior may be qualitatively applicable.

A complete explanation of viscosity anomalies must consider Brownian movement, which competes with the orienting and stretching forces and renders them less effective at higher temperatures. The absence of non-Newtonian effects in the viscosity experiments on polyisobutylene by the falling sphere method is attributed to the considerable thermal agitation at those temperatures and to the low shearing stresses involved in the flow.

It would be desirable, in anticipation of an adequate theory of viscous behavior, to make a complete experimental study of the dependence of elastic and viscous flow on time, shearing stress, and temperature, using preferably a one-component system, of which many glass-forming liquids offer convenient examples.

Compressional Waves in Media with Complex Viscosity

A. GEMANT, *Engineering Laboratory, Oxford University*

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The author recently suggested the introduction of a complex viscosity in the theory of vibrations of materials which lie between the purely crystalline and the liquid state. This conception is utilized here in the theory of compressional waves in an infinite medium. One of the conclusions, namely, the decrease of the attenuation factor with increasing frequency, is in agreement with observations. Another conclusion is an increase of the propagation velocity with frequency. Both changes occur in the neighborhood of a certain characteristic frequency, given by the reciprocal of the so-called relaxation constant. Below this frequency range the material vibrates like a liquid; above this range like a crystal.

THE behavior of a medium with regard to longitudinal compressional waves is generally described by means of two constants. One of them is the velocity of propagation, c, the other the attenuation factor, α. Apart from a term in the latter caused by heat conduction, α is proportional to the viscosity of the medium, μ. This viscosity can be calculated from the attenuation factor, and the agreement between this value of the viscosity and its value known from other determinations is usually satisfactory, at least in order of magnitude. Such is the case with measurements concerning gases and liquids. Usually these media are dealt with since they allow the conditions corresponding to propagation of waves in an infinite medium to be reproduced satisfactorily. Even more frequently they are investigated in tubes, since the theory of waves in tubes is well developed.

More difficult is the investigation of solids, as their finite shape, that is the consideration of the boundary conditions, makes the evaluation of measurements rather complicated; correspondingly, only a small amount of data is available. It seems, however, that such measurements show a certain discrepancy between theory and experiment. In the first place, the derived value of the viscosity is much lower in order of magnitude than the static value. Secondly, the viscosity seems to decrease with increasing frequency of the waves.

For example, J. H. C. Thompson[1] compares the values for μ obtained by several authors for metals and glass, as follows: Hettwer[2] obtained with very slow torsional vibrations the order 10^{15}, an order probably not far from the static value. Honda and Konno,[3] investigating the torsional pendulum at higher frequencies, found the order 10^{8}. S. L. Quimby[4] applied ultrasonic vibrations set by a quartz oscillator to solid rods and derived for μ the order 10^{3}. The decrease of the order of the viscosity with increasing frequency is very definite and especially the last order obtained by Quimby is much lower than the static value.

Crandall[5] mentions in his *Vibrating Systems and Sound* unpublished experiments of P. W. Bridgman and H. M. Trueblood, who investigated the propagation velocity and damping of sound waves in rubber. They also observed qualitatively a behavior similar to that described above.

In a recent paper, J. C. Eccles and J. H. C. Thompson[6] measured the damping of longitudinal vibrations in rubber for frequencies of the order 10^{2}. The value for μ as calculated for pure black rubber ranges from 8.10^{3} for a frequency 16, to 5.10^{3} for a frequency 32. The order for μ is again certainly lower than that of the static value. The order 3.10^{3} is that of the static viscosity of a rather viscous oil, as can be seen from measurements of the author.[7] This value was observed for some lubricating oils at 0°C; the static value for rubber must be considerably higher.

These peculiarities can be explained by a

[1] J. H. C. Thompson, Phil. Trans. Roy. Soc. **A231**, 339 (1933).

[2] Hettwer, Wien Ber. **134**, 51 (1925).

[3] Honda and Konno, Phil. Mag. **42**, 115 (1921).

[4] S. L. Quimby, Phys. Rev. **25**, 559 (1925).

[5] I. B. Crandall, *Vibrating Systems and Sound* (Van Nostrand Co., 1927), p. 111.

[6] J. C. Eccles and J. H. C. Thompson, Proc. Roy. Soc. **A148**, 171 (1935).

[7] A. Gemant, *Viskosität u. Fliessfestigkeit* Berl. Ber. (1932).

theory suggested recently by the author.[8, 9] The idea of this theory was given by considerations of a somewhat analogous peculiarity of the viscosity in the field of certain organic colloids, generally called elasto-viscous liquids. In order to explain their behavior, the Maxwellian conception of elasto-viscosity has been applied to them by H. Hencky[10] and others with considerable success. The theory of the author is a generalization of this idea. The generalization is twofold. Instead of assuming a viscous resistance and a resilience connected in parallel, as in the original conception, it is assumed that the damping term is the resultant of a more complicated combination of units, and that it consists in the simplest case of three elements at least. Such units are known from the treatment of plastic bodies.[11] This combination will be called the complex viscosity and denoted by V.

The second generalization refers to the application. It can be applied to any kind of vibration in viscous media. Thus the application to the flow of liquids, as has been done by Hencky and others, is only one possibility. Another application is concerned with electric losses in amorphous solid dielectrics, giving an extension of the theory of Debye[12] to such materials. This extension has been carried out quantitatively in one of the above-quoted papers.[9]

A third application is concerned with the acoustical waves in solids, the attenuation of which cannot be explained on the basis of a simple viscosity constant μ, as has just been pointed out.

In this note only the simplest case, really the fundamental one, is discussed, namely, the damping of waves in a laterally unlimited isotropic medium. Another important case, namely, waves in a medium contained in a rigid circular tube, will be treated in another communication. Again, the case of vibrations in a solid bar needs separate treatment.

In order to fix our ideas, it should be recalled that V is considered in the simplest case as a parallel combination of a viscous resistance η_0, on the one hand, and of a series combination of a resilience E and another viscous resistance η, on the other. Here η_0 is the static viscosity and corresponds physically to an agitational displacement of molecules, such as is generally assumed to take place in liquids. E is the elastic resistance to a regular displacement of molecules without disturbance of their structure, a motion which characterizes displacements in crystals. η is the frictional resistance to be overcome during this crystalline displacement. In a so-called Newtonian liquid η_0 is so small that the other branch in V becomes unimportant; in a crystal, on the other hand, η_0 is so large that only the branch $E-\eta$ is of importance. The general complex impedance covers therefore the whole transition state between a pure liquid and a pure crystal. To this state belong all the amorphous or glassy materials, and all those which can be considered (in a certain temperature range) as a colloidal mixture of crystalline *and* liquid or glassy constituents (paraffin wax, for instance).

The quantity $$\tau_0 = \eta_0/E \tag{1}$$

is called the visco-elastic time constant of relaxation for reasons shown below. It is easy to show[9] that V may be expressed as a complex quantity:

$$V = \eta' - iE'/\omega, \tag{2}$$

where ω is 2π times the frequency. Both η' and E' are dependent on frequency. Considering that in all practical cases

$$\eta_0 \gg \eta, \tag{3}$$

we get for η' with good approximation:

$$\eta' = \eta_0[1+(\eta/E)\tau_0\omega^2]/[1+(\tau_0\omega)^2] \tag{4}$$

and for E': $$E' = E(\tau_0\omega)^2/[1+(\tau\omega)^2]. \tag{5}$$

It may be seen that for frequencies below $1/\tau_0$, η' becomes η_0 and E' very small, whereas for frequencies above $1/\tau_0$, η' becomes η and $E' : E$. This is the reason why τ_0 is called the time constant of relaxation; the transition from an original elastic strain to a viscous flow takes place in an interval of the order τ_0.

We have to apply Eq. (2) to the theory of propagation of longitudinal waves. Denoting the

[8] A. Gemant, Naturwiss. **23**, 406 (1935).
[9] A. Gemant, *Conception of a Complex Viscosity and its Application to Dielectrics*, Trans. Faraday Soc., in press.
[10] H. Hencky, Ann. d. Physik **2**, 617 (1929).
[11] First Report on Viscosity and Plasticity, Acad. of Sciences at Amsterdam, 1935.
[12] P. Debye, *Polar Molecules* (New York, 1929).

displacement in the direction x by ξ, the velocity by $\dot{\xi}$, we have:

$$\rho\frac{\partial^2\xi}{\partial t^2}-\frac{4}{3}\mu\frac{\partial^2\xi}{\partial x^2}-\kappa\frac{\partial^2\xi}{\partial x^2}=0, \tag{6}$$

where ρ=density and κ=bulk modulus of elasticity.

(6) is the classical equation derived by H. Lamb. Since the quantity V, which has to replace the simple viscosity μ is a complex one, Eq. (6) has to be brought to a complex form. This is done by assuming for the solution:

$$\xi=\xi_0 e^{i\omega(t-x/c_1)}, \tag{7}$$

where c_1=complex propagation constant.

In substituting (7) in (6), we obtain

$$-\rho+i(4/3)\mu\omega/c_1^2+\kappa/c_1^2=0. \tag{8}$$

Now μ has to be replaced by V, and we get:

$$-\rho+i(4/3)\eta'\omega/c_1^2+(4/3)E'/c_1^2+\kappa/c_1^2=0,$$

hence $$c_1^2=(\kappa/\rho)(1+(4/3)E'/\kappa+i(4/3)\eta'\omega/\kappa).$$

If the damping term is small compared with the others, we have to a first approximation:

$$c_1=\left[\frac{\kappa}{\rho}\left(1+\frac{4}{3}\frac{E'}{\kappa}\right)\right]^{\frac{1}{2}}\left(1+\frac{i\frac{2}{3}\eta'\omega/\kappa}{1+(4/3)E'/\kappa}\right). \tag{9}$$

The complex expression for c_1 permits calculation of the real propagation velocity and the attenuation factor. Since (7) is identical with

$$\xi=\xi_0 e^{-\alpha x}e^{i\omega(t-x/c)}, \tag{7a}$$

we have the identity:

$$c_1=c(1+i\alpha c/\omega). \tag{10}$$

Comparing (10) with (9), we have for c,

$$c=[(\kappa/\rho)(1+(4/3)E'/\kappa)]^{\frac{1}{2}}, \tag{11}$$

and for α: $$\alpha=\tfrac{2}{3}\eta'\omega^2/\rho c^3, \tag{12}$$

where E' and η' are given by (4) and (5).

The following conclusion can be drawn from these equations. For $\omega<1/\tau_0$: $E'\ll E$ and $\eta'=\eta_0$. Since E is of similar order to κ, this means that $c=(\kappa/\rho)^{\frac{1}{2}}$ and $\alpha=\frac{2}{3}\eta_0\omega^2/\rho c^3$. These equations are the same as obtained by considering the medium as a liquid with bulk elasticity κ and viscosity η_0. Below the critical frequency the medium behaves like a liquid.

For frequencies $\omega>1/\tau_0$, we have $E'=E$ and $\eta'=\eta$. Hence

$$c=[(\kappa/\rho)(1+(4/3)E/\kappa)]^{\frac{1}{2}},$$

and $$\alpha=\tfrac{2}{3}\eta\omega^2/\rho c^3.$$

The medium here behaves like a crystal. The bulk elasticity is now $(\kappa+4E/3)$, a quantity which includes the elasticity owing to lattice distortion, as defined by (2). The damping is given by the dissipation accompanying crystal distortion. If E is small compared with κ, the change in c may be only a second-order effect.

The transition between the two cases just considered occurs continually in the frequency range $\sim 1/\tau_0$. Now in a number of cases, especially with solids, such as glass at room temperature, τ_0 is certainly larger than 1 sec. In other cases, like rubber, it might be less than 1 sec. For liquids showing structure viscosity it is certainly considerably smaller than 1 sec. The range in which the greatest variation of the propagation velocity (i.e., the most pronounced dispersion of waves) and of the attenuation factor is to be expected depends on the value of τ_0.

Whereas the theory seems to explain the above-mentioned peculiarities satisfactorily, a quantitative check would require more experimental data. It should be added only that the experimental curve relating the variation of damping with frequency is probably more flat than indicated by (4). This would mean that the simple equivalent circuit as accepted for V is not adequate. There are experimental indications for the exponent of the argument $(\omega\tau_0)$ in Eqs. (4) and (5) being nearer to unity.

From the standpoint of comparison with experiment, the extension of the theory to propagation in tubes and to vibration of bars is of great importance.